Establishing the potential dependent equilibrium oxide coverage on platinum in alkaline solution and its influence on the oxygen reduction

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HIGHLIGHTS

► A procedure for studying Pt under quasi steady state conditions is introduced.
► We determine different potential regions of oxide formation.
► A clear correlation between OH adlayer formation and inhibition of the ORR is shown.

ARTICLE INFO

ABSTRACT

The oxidation process of polycrystalline platinum subjected to alkaline solution is re-examined using a combination of cyclic voltammetry and potential hold techniques in Ar, H_2 and O_2 purged 0.1 M KOH solution. The hydrogen oxidation reaction is used as a probe for forming a complete OH adlayer, whereas the comparison of cyclic voltammetry with potential hold techniques allows the investigation of the dynamics as well as a charge balance of the processes. Comparing the different findings in a parameterized form, we are able to discern the potential regions of OH and O adlayers as well as PtO formation at quasi steady state conditions: only low amount of OH exists up to 0.7 V_{RHE}. Increasing the potential the OH coverage increases and a OH monolayer is formed at 0.93 V_{RHE}, which gradually further oxidizes to O_{ad} increasing the potential up to 1.08 V, above which PtO oxide is formed. Comparing the oxidation process to the oxygen reduction reaction it is shown that there is a clear correlation between the formation of a full OH adlayer and the inhibition of the oxygen reduction.

1. Introduction

Platinum is extensively studied in electrochemistry because of its high catalytic activity towards the oxygen reduction reaction (ORR) and hydrogen oxidation reaction (HOR). Although Pt is considered to be one of the most active metals for these reactions, the ORR nevertheless exhibits a significant overpotential of more than 0.2 V, i.e. oxygen reduction currents are only observed below 1.0 V_{RHE}. In fact the overpotential for the ORR is one of the main inhibitors for large scale applications of low temperature fuel cells with acidic electrolytes as it reduces the efficiency of the conversion of chemical into electrical energy. In alkaline solution, the kinetics of the HOR are inhibited as well and pose an additional overpotential to the overall reaction in alkaline fuel cells. Thus studies on the nature of the ORR and HOR overpotentials are both of fundamental as well as applied interest.

In previous experimental studies of the ORR on Pt, on the basis of its pH dependence and the comparison of Tafel slopes it was concluded that the first charge transfer to the oxygen molecule is the rate determining step (rds) [1–3]. Furthermore, it was assumed that at low overpotentials the surface coverage of oxygen intermediates affects the activation energy of the process while at high overpotentials its influence becomes negligible. Later the concept of intermediates affecting the reaction rate was extended to the influence of spectator species, i.e. species not directly involved in the reaction but co-adsorbed on the surface and thus blocking reaction sites [4]. A typical example for such a spectator species is the co-adsorption of chloride anions from the the electrolyte [5]. In this respect the adsorption of OH exhibits a special role for the ORR in aqueous solutions. OH_{ad} may be formed directly from water and act as a spectator species or it is a reaction intermediate during oxygen reduction. Recent theoretical descriptions of the ORR based on density functional theory (DFT) calculations by Norskov et al.

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indicate that water dissociation and the ORR are indeed two sides of the same phenomenon [6,7]. Indifferently whether the oxide species (adsorbed oxygen atoms or hydroxyl) originate from water dissociation or oxygen molecules, the strong interaction with platinum at potentials close to the reversible potential impedes the proton and electron transfer. Only by lowering the potential, the stability of the oxygen bond decreases and the ORR may proceed. In other words, the key to understand the ORR is to elucidate the reduction of platinum oxide species and its potential dependent equilibrium coverage.

The scope of the presented study is to re-examine the reduction of platinum oxides in alkaline solution and its influence on the ORR using different electrochemical techniques. Our approach to probe the surface by investigating the HOR and ORR in stripping voltammetry applied after potential holds. By comparing the resulting key indicators detailed insight is gained regarding the equilibrium coverage of different oxygenated species adsorbed on the Pt surface.

2. Experimental

All electrochemical measurements were conducted in a home build 3-compartment Teflon cell [8,9]. The electrolyte solutions 0.1 M $HClO_4$ and 0.1 M KOH were prepared using Millipore water (Resistivity = 18.2 $M\Omega$ cm^{-1}, TOC < 5 ppb), concentrated $HClO_4$ and KOH pellets (Merck, Suprapure). During measurements, the electrolyte was saturated either with argon, carbon monoxide, oxygen or hydrogen. As reference electrode, a Mercury–Mercury oxide electrode was employed, however, the reversible potential of hydrogen oxidation/reduction was experimentally determined for each measurement, and all presented data are given with respect to the reversible hydrogen electrode (RHE). The working electrode was a polycrystalline (PC) Pt disk (Ø = 5 mm, A = 0.196 cm^2) mounted into a Teflon RDE tip. The disk was cleaned by polishing, inserted into a sonic cleaner and finally inserted for 5 min in concentrated $HClO_4$.

Prior to each experimental series, the Pt electrode was cycled in CO saturated perchloric acid (CO annealing) in a separate cell in order to obtain reproducible surface conditions [10,11]. The electrode was thereafter rinsed in Millipore water and finally inserted into the cell containing KOH solution. The solution resistance between the working electrode and the Luggin capillary [12] was determined using an AC signal (5 kHz, 5 mV), and thereafter electronically compensated for using the positive feedback scheme of the home-built analogue potentiostat [13,14]. The resulting effective solution resistance was 2 Ω for each experiment. All experiments were performed at room temperature.

3. Results and discussion

Cyclic voltammetry (CV) performed in Ar saturated electrolyte is usually used for a first, basic characterization of electrode processes. Thereby often the scan rate v is kept constant. CV can further be a practical tool for the characterization of the dynamics of adsorption/desorption processes as the currents that are related to adsorption/desorption processes are proportional to the scan rate. Therefore, recording CVs at different scan rates and plotting the measured current density j normalized to v one expects that fast processes overlap, whereas current peaks associated with slower processes shift with changing the scan speed.

In Fig. 1, it is demonstrated how the adsorption/desorption peaks in the CVs of Pt recorded in Ar saturated 0.1 M KOH solution change with increasing the scan rate. The CV recorded at low scan rate (0.10 V s^{-1}, see Fig. 1) is well known. In the underpotential deposition region of hydrogen (H_{upd}) between 0.05 and 0.5 V_{RHE}

two well defined peaks evolve due to the adsorption/desorption of hydrogen atoms at different facets of the polycrystalline Pt crystal. The pseudocapacity between 0.5 and 0.7 V_{RHE} is traditionally ascribed to charging and de-charging of the electrochemical double layer close to the surface. Beginning at 0.7 V_{RHE} in the positive going sweep a peak arises, which is usually associated with the adsorption of oxygenated species (OH_{ad} or O_{ad}). The peak positions of the surface oxidation/reduction in the positive and negative going scan are − dependent on the positive potential limit − shifted to each other (not shown) and therefore the surface oxidation process is often considered not to be reversible. In Fig. 1 it is demonstrated that when limiting the positive potential limit to 1.06 V_{RHE} the peak position at 0.8 V_{RHE} in the CV, both in positive and negative scan direction, is independent of the scan rate up to very high rates (≤10 V s^{-1}) indicating a fast reversible process. At the same time the peaks correlating to the H_{upd} process merge together with increasing scan rates and shift to more positive/negative potentials in the positive and negative going sweep, respectively. This is a clear indication of a rather sluggish process. These observations obtained by CV are in agreement with previous investigations by impedance spectroscopy [15,16] − a technique often used for the investigation of dynamic processes. It is noteworthy that for studying fast dynamics of surface processes by CV a full in-situ compensation of the solution resistance in the electrochemical cell is essential during the measurements. Correction for the solution resistance after the measurement, as sometimes performed, is not suitable as it also affects the effective scan rate [13]. In any case the scan speed dependent CVs clearly indicate that the initial oxidation of the Pt surface in alkaline electrolyte and its reduction are relatively fast processes, whereas the H_{upd} process by comparison is rather sluggish. The latter fact might be connected with the sluggish HOR on Pt in alkaline solution [17].

Furthermore, the CV series reveals that although the peaks at 0.8 V_{RHE} do not shift with the applied scan rate, the normalized magnitude of the peak current decreases as the scan rate increases, indicating that the full equilibrium oxide coverage may not be reached instantaneously. This seemingly contradicting behaviour to a fast adsorption process might be explained by a slower ordering process of the adlayer to reach full equilibrium coverage.

An additional tool for the characterization of the adsorption of oxygenated species on Pt is to probe its influence on the catalytic oxidation of hydrogen (HOR). The decrease of the HOR at high potentials is well known. Bao et al. recently interpreted this
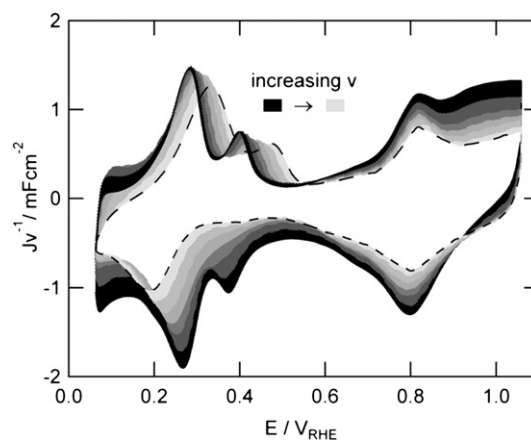
Fig. 1. Series of cyclic voltammograms of polycrystalline Pt. The CVs are recorded at scan rates ranging from 0.1 to 10 V s^{-1} (black to light grey; the dashed curve is the CV at 10 V s^{-1}) in Ar saturated 0.1 M KOH solution and are plotted normalized to the scan rate.

decrease as a decline in the "tunnelling current" of electrons through a growing isolating oxide layer [18]. However, considering that the HOR is a catalytic reaction and not a Helmholtz reaction, the probing capability of the oxide thickness by the HOR is questionable. Instead, the decrease in the HOR rate can be interpreted as a decrease in available active sites due to blockage of the Pt surface by adsorbed oxygenated species [19]. Keeping in mind that the HOR can continue (in acid electrolyte) to be diffusion limited up to a partial surface coverage of blocking species of 90% [20], a direct correlation of the measured current to the number of free sites cannot be extracted without the knowledge of the exact oxide growth formation and the required sites for the reduction of hydrogen. Such a model is lacking so far. Consequently, the microscopic information provided by the potential dependence of the HOR is limited. However, the absence of any HOR current distinctively indicates a completely blocked surface.

In order to analyze the polarization curves recorded in hydrogen saturated electrolyte, one needs to separate the contributing current of the HOR and that induced by the oxide formation/reduction to the measured current. To do so we use the fact that, as discussed before, the oxide formation currents are proportional to the scan rate whereas currents related to the HOR are independent of the scan rate as it is a fast continuous faradaic reaction. In the same manner as the CVs in Ar saturated electrolyte, the HOR is recorded as a function of the scan rate, see Fig. 2A where polarization curves recorded in hydrogen saturated 0.1 M KOH solution are compared for scan rates between 0.05 and 1 V s^{-1}.

At low scan rate (black area in Fig. 2A; $v = 0.05$ V s^{-1}), the polarization curve exhibits mainly the well known characteristics of a continuous faradaic process, i.e. close to the reversible potential of the HER/HOR (0.00 V$_{RHE}$), the measured current density is controlled by the kinetics of the hydrogen oxidation, whereas in the potential region $0.1 < E < 0.8$ V$_{RHE}$, it is limited by mass transport, i.e. the convection/diffusion of hydrogen to the surface. Above 0.8 V$_{RHE}$ the current density decreases until around 1.0 V$_{RHE}$ where it almost reached zero, corresponding to the oxidation of the Pt

surface indicated in the CV recorded in Ar saturated electrolyte (Fig. 1). Note also the hysteresis in the polarization curve (i.e. the difference between positive and negative going sweep) in the oxide region, in contrast to the region around the reversible potential. Superimposed on these faradaic currents, very small features of the adsorption and desorption of hydrogen are discernible in the polarization curve. Increasing the scan rate up to 1 V s^{-1} (dashed curve), however, the superimposed H_{upd} and platinum oxidation features appear more clearly. Note especially the peak appearing at 0.8 V$_{RHE}$. In order to extract these surface features, a polarization curve recorded at low scan rates was subtracted from the measurements at higher scan rates. This is shown in Fig. 2C where parts of the positive scan for different scan rates (0.2–1 V s^{-1}) are plotted after subtraction of a curve recorded at 0.05 V s^{-1}. For comparison, normalized CVs recorded at corresponding scan rate in Ar saturated solution can be seen in Fig. 2D. It is apparent that the peak position and height of the Pt oxidation features are the same in the two graphs. This indicates that HOR does not interfere with the oxidation of the surface and the current responses of two processes indeed can be separated.

The rate of the HOR can be extracted from the polarization curves shown in Fig. 2A by subtracting a CV recorded at corresponding scan rate in Ar saturated solution. The results are displayed in Fig. 2B. Focussing on the oxide region, it is observed that the resulting curves of the positive potential sweep (0.05–1 V s^{-1}) are almost independent of the scan rate. In contrast, the curves of the negative potential sweep exhibit a hysteresis which becomes more pronounced as the scan rate decreases. This finding is a further indication that the equilibrium oxide coverage is not reached instantaneously.

In order to probe the free surface sites by the HOR, the presence of H_2 in the electrolyte should not interfere with the formation of surface oxides. Our results presented in Fig. 2 demonstrate that this is indeed the case and that the current contributions of both processes can be separated from each other.

The results show further that in conventional cyclovoltammetry, the oxide coverage is not at equilibrium, and hence the chosen scan rate as well as upper potential limit affect the current response, especially in the negative going potential sweeps. In order to obtain steady state conditions, it would be necessary to decrease the scan rate to very low values (<1 mV s^{-1}). This however is not feasible as the measured signal from surface reactions would be very small as well as easily be subject to artifacts and contaminations from the electrolyte. Therefore, in order to probe the surface oxidation state at equilibrium conditions, a stripping technique is more adequate. By holding the potential at a fixed value (E_d) in the region of oxide formation for an adequate time (here potential holds of 100 s are applied) a quasi steady state oxide coverage is reached. The following linear sweep voltammetry starting at E_d towards more negative potentials gives a reduction peak which can be correlated to the equilibrium oxide coverage on the electrode. In order to distinguish the negative going linear sweep after the potential hold from the consecutive positive going linear potential sweep we denote them as sLSV and pLSV, for stripping and positive going linear sweep voltammetry respectively.

The results of such a stripping procedure performed in Ar saturated solution are shown in Fig. 3. As can be seen, the recorded sLSV are sensitive to the deposition potential, whereas the consecutive pLSV all coincide. In the sLSV the magnitude of the oxide reduction peak, its integrated area (Q_{ox}), and its peak potential (E_{pp}) change as a function of the hold potential E_d. A similar behaviour was reported for investigations performed in acid solution [21]. Interestingly in alkaline solution, for a wide range of hold potentials ($E_d = 0.93$–1.08 V$_{RHE}$) the peak potential E_{pp} of the sLSV reduction curves stays constant (see also Fig. 5) indicating
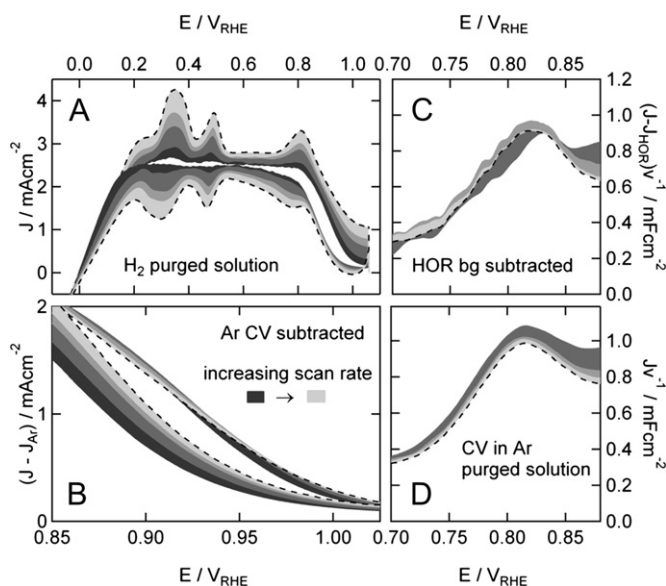

Fig. 2. Polarization curves of polycrystalline Pt recorded at 1600 rpm and different scan rates between 0.05 and 1 V s^{-1} (dashed line) in 0.1 M KOH solution saturated with hydrogen (A). (B) parts of the polarization curves after subtraction of the respective CV recorded at same scan rate in Ar saturated solution. (C) parts of the positive going scans after subtracting the HOR polarization curve recorded at 0.05 V s^{-1}. (D) parts of the CV curves recorded in Ar saturated solution (from Fig. 1).
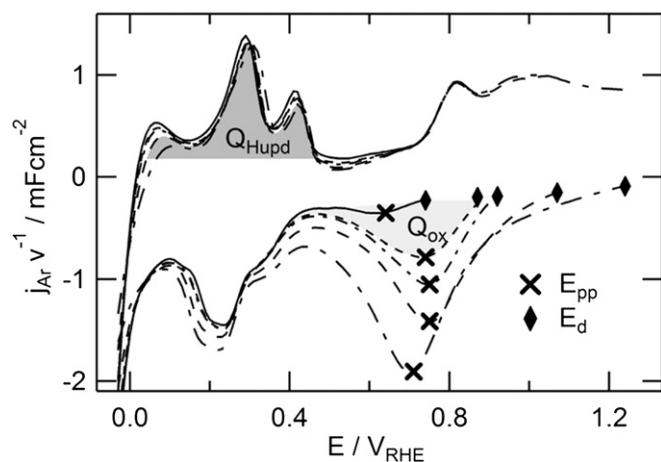
Fig. 3. Negative going linear potential sweep (sLSV) after potential hold for 100 s and consecutive positive going linear potential sweep (pLSV) of polycrystalline Pt for different hold potentials E_d. The curves are recorded with 0.5 V s^{-1} in argon saturated 0.1 M KOH solution at a rotation rate of 1600 rpm. For a better comparison the currents in the plot are normalized to the scan rate and the Pt surface area. Key features have been highlighted: charge integration of the oxide peak (Q_{ox}) and H_{upd} features (Q_H) as well as the oxide reduction peak position (E_{pp}).

a special significance of these two potential values. The charge under the H_{upd} peaks in the sLSV is also affected by the hold potential. Even though the effect is only minor, this indicates that to some extent oxide species are still being reduced in the H_{upd} region in the negative going scan and thus co-exist with adsorbed hydrogen atoms in agreement with CO oxidation studies [22]. In the subsequent pLSV, however, the total charge determined from integrating the H_{upd} peaks, labelled as Q_H, is unaffected by the hold potential indicating that in the preceeding sLSV scan all oxide was reduced.

In order to further investigate the oxide formation/reduction process on polycrystalline Pt, the same stripping procedure as in Ar saturated solution was applied while probing the HOR in hydrogen saturated solution. The results are summarized Fig. 4. The sLSV
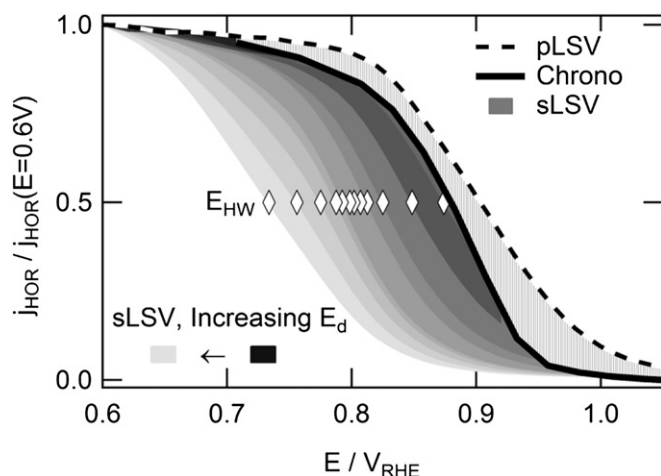
Fig. 4. sLSV curves of polycrystalline Pt recorded after different hold potentials $E_d = [0.7–1.25 \text{ V}_{RHE}]$; the curves are coded in grey colours, the grey gets lighter with increasing E_d; all curves were recorded in H$_2$ saturated 0.1 M KOH solution; the scan rate was 0.5 V s^{-1}, the rotation rate 1600 rpm. Furthermore the subsequent pLSV is shown (black dashed line) and the current after the potential hold (black solid line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
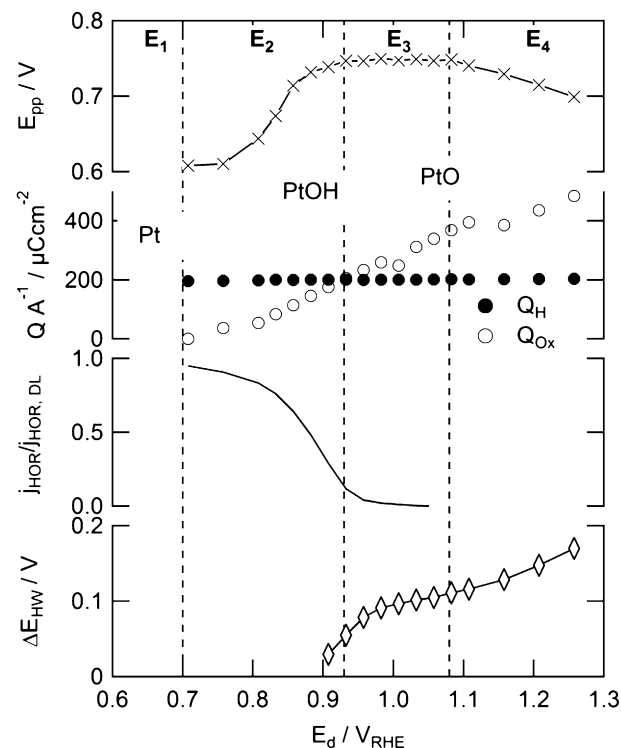
Fig. 5. The peak potential E_{pp} of the reduction of adsorbed oxygenated species observed in CVs recorded in Ar saturated electrolyte is compared to its the calculated stripping charge (Q_{Ox}) and the H_{upd} charge (Q_H) obtained in the same measurement. Furthermore the normalized steady state HOR current and the difference between the half wave potentials of sLSV and pLSV measurements in H$_2$ saturated solution are shown. All values are given as a function of the hold potential E_d.

polarization curves recorded after the potential hold are indicated by the grey scale (towards lighter grey with increasing hold potential E_d), whereas the coinciding pLSV curves of the subsequent positive going scans are represented by the dashed line. Furthermore, the steady state HOR current density after 100 s is marked by the thick black line (chrono) and the decrease in HOR current density upon stopping the potential scan and holding the potential fixed for 100 s is displayed by the dashed area. In order to simplify their comparison all currents have been normalized to the diffusion limited current at 0.6 V$_{RHE}$ and the current contribution from the surface oxidation process has been subtracted as discussed before.

Analyzing the results it is evident that stopping the potential only leads to a decrease in the HOR current for values $E_d > 0.7$ V$_{RHE}$. Below this potential value the HOR currents are not affected, i.e. only above 0.7 V$_{RHE}$ the steady state surface oxidation is not sufficient to partially block the HOR. Furthermore, a complete blocking of the Pt surface, i.e. zero HOR current after 100 s, is reached at potentials $E_d > 0.95$ V$_{RHE}$.

In accordance with the stripping experiments in Ar saturated electrolyte also the HOR measurements indicate that reaching the steady state oxide coverage is a slow process and at too high potentials the oxidation process becomes less reversible. For hold potentials above 0.85 V$_{RHE}$ the sLSV polarization curves start to shift to lower potentials upon increasing the hold potential. In other words, the higher the potential value at which the potential is hold for 100 s, the less reversible the blocking effect becomes and a lower potential is needed in order to reduce the oxide species. This behaviour is best characterized by the half wave potential (E_{HW}) of the HOR. Fig. 4 shows how E_{HW} shifts with increasing the hold potentials. Assuming that the activity at the half wave of the

HOR polarization curve corresponds to similar surface conditions, although unknown as previously discussed, the shift of the E_{HW} can be seen as an indicator of the changing state of a growing monolayer as E_{HW} would be constant for a reversible reaction. For a coverage of more than a monolayer at E_d, E_{HW} would shift negatively as well as it takes more time in the sLSV scan to reduce the oxide.

In the following we try to interpret our findings and summarize them before putting them into a context to the ORR. Based on the CVs recorded in Ar saturated solution, it is shown that the initial oxidation of the Pt surface is a fast process. The surface oxidation/reduction peak at 0.8 V_{RHE} is reversible and no peak shift is discernible even at scan rates as high as 10 V s^{-1}. However, the complete surface oxidation, i.e. the filling of the surface, takes some time. Thus if the system prolonged for 100 s at a high positive potential, the reduction peak in the concomitant sLSV curves in Ar saturated solution shift significantly (≈ 70 mV) towards more negative potentials (see Fig. 3). The HOR exhibits an analogue behaviour. Comparing positive and negative going scan directions of the polarization curves, a hysteresis is discernable which increases with decreasing the scan rate (Fig. 2). Using the stripping procedure for the HOR and comparing the negative going sLSV to the positive going pLSV curves, the described effect becomes even more evident (Fig. 4).

Let us now compare these findings in a parameterized form. In Fig. 5 the characteristic values from the stripping voltammetry in argon and hydrogen saturated alkaline solution are plotted as a function of the hold potential E_d. In the upper part the peak potential E_{pp} of the sLSV curves recorded after potential hold in argon saturated solution is shown and below compared to the corresponding charges Q_{Ox} and Q_H of the reduction peak and H_{upd} peak. In addition the normalized current densities of the steady state HOR polarization curve and the difference ΔE_{HW} in the half wave potentials of sLSV and pLSV HOR curves are shown.

According to the results shown in Fig. 5, the coverage of oxygenated species on the platinum surface can be divided into 4 potential regions, i.e. $E_1 < 0.7$–0.93 V_{RHE} (E_2) < 0.93–1.08 V_{RHE} (E_3) $< E_4$. In the low potential region E_1 the oxygenated species can be assumed to be OH. Its coverage is relatively low, neither inducing an unambiguous reduction peak in the potential hold experiments nor inhibiting the HOR; however enough to sustain continuous CO oxidation [22]. The subsequent potential region E_2 is characterized by the decrease of the HOR as well as the shift of E_{pp} with increasing hold potential. We interpret this behaviour with the completion of an OH adlayer on Pt; a process which according to the comparison of Q_{Ox} and Q_H is completed at 0.93 V_{RHE} and only inflicts a minor hysteresis in HOR, i.e. ΔE_{HW} is negligible.

Upon completion of the OH adlayer, i.e. above 0.93 V_{RHE} no steady state HOR current is measured indicating the complete blockage of all Pt sites. Q_{Ox} exceeds Q_H which indicates either the formation of a Pt(OH)$_2$ or an O adlayer. Interestingly, in this potential region (E_3) E_{pp} stays constant, whereas ΔE_{HW} first increases and then slightly saturates. In the potential region E_4 above 1.08 V_{RHE}, a negative shift of the peak potential E_{pp} of the oxide reduction is seen with increasing the hold potential in combination with a further increase of ΔE_{HW}. The oxide formed in this potential range is present on the surface also in the Hupd region as demonstrated in Fig. 3 by the increased reduction current. These findings and the fact that $Q_{Ox} > 2Q_H$ are a clear sign that a less reversible oxide layer starts to form after the first O$_{ad}$ monolayer [23] or a Pt(OH)$_2$ layer. Most probably the process involves site exchange processes of O with Pt atoms which irreversibly can roughen the surface [24]. The formation of oxide multilayers has also been reported using other techniques. Electrochemical quartz-crystal nanobalance (EQCN) experiments have shown an increase

of 16 gmol^{-1} e$^-$ in the oxide region [25,26]. The onset of a more stable oxide was identified by the change of signal stability of the oxide upon exposure to an electron beam [25] as well as clear change of surface morphology of Pt [111] using in-situ STM [27].

The nature of the oxide layer in the different potential regions is intriguing. At $E_d = 0.93$ V_{RHE}, Q_{ox} becomes equivalent to Q_H while the HOR reaction is almost totally inhibited. This complete blockage of the HOR indicates that below 0.93 V_{RHE} only a very limited amount of PtO species can be adsorbed. Otherwise, it would be expected from the charges that sufficient free sites for the HOR are present on the surface. Assuming for example a pure PtO layer, at 0.93 V_{RHE} a maximum coverage of 50% is reached based on Q_{ox} [28]; certainly not enough to inhibit the HOR. Wakisaka et al. performed potential hold experiments on Pt(111) and PC Pt in HF solution with subsequent X-ray photoelectron spectroscopy in a vacuum chamber [29]. They ascribed adsorbed species with different bonding energies to OH$_{ads}$ and O$_{ads}$. Their occurrence on the surface was plotted as a function of potential for both Pt(111) and polycrystalline Pt surface. Their results for Pt(111) corresponds well to our results, however, that of the polycrystalline Pt assume an equal adsorption of OH$_{ads}$ and O$_{ads}$ starting at 0.8 V_{RHE}. This disagreement to our findings might be attributed to the fact that their measurements are performed ex-situ and in acid electrolyte whereas in the current study in-situ investigations were performed in alkaline solution and no emersion of the sample out of the electrolyte was necessary like in vacuum studies. Furthermore, the different preparation method of our sample, i.e. CO annealing, is known to reduce surface defects [30]. The oxidation of Pt(111) by gas phase oxygen atoms has been studied by Weaver et al. [31]. They proposed that O$_{ad}$ exhibits a repelling interaction at low coverage and first a chemisorbed layer of oxygen atoms growths. Once the coverage exceeds 0.75 ML, the growth of platinum oxide commenced which is energetically more stable than chemisorbed atoms. Relating this work to our results, around the potential where a monolayer of OH is formed, the oxide layer exhibits a change in its
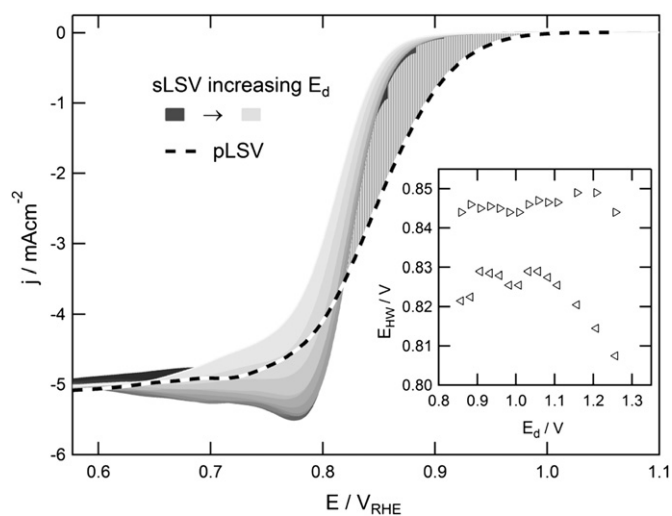
Fig. 6. sLSV curves of polycrystalline Pt recorded after different hold potentials $E_d = [0.85$–1.25 $V_{RHE}]$; the curves are coded in grey colours, the grey gets lighter with increasing E_d; all curves were recorded in O$_2$ saturated 0.1 M KOH solution; the scan rate was 0.5 V s^{-1}, the rotation rate 1600 rpm. Furthermore a single representative subsequent pLSV curve is shown as black dashed line (the pLSV curves overlap). In the inset the half-wave potentials E_{HW} of the ORR polarization curves are plotted as a function of the hold potential E_d. The apex of the triangles points towards the scan direction; i.e. the triangles pointing to the left belong to the sLSV curves, whereas the triangles pointing to the right belong to the pLSV curves. The fact that the latter are constant at around 0.845 V_{RHE} demonstrates the independence of pLSV from the hold potential.

behaviour. A rapid shift (ΔE_{HW}) in the E_{HW} of the sLSV and pLSV curves of the HOR emerges indicating a less reversible behaviour of the oxide film around the formation of a monolayer of OH. Therefore, we suggest that the growing adlayer on platinum undergoes a slow phase transition also in aqueous medium in the potential region E3 where OH_{ad} is gradually transformed into O_{ad}. Furthermore, the observed 70 mV shift between the reduction peak position of the CV and sLSV suggests that the OH_{ad} layer has stabilized if given enough time (100 s). These effects would be the predominating in causing the HOR hysteresis that is both depending on the upper potential and the scan rate during a CV.

We will now put these potential regions in context to the ORR. In Fig. 6 the same potential hold experiments as recorded in hydrogen saturated solution are shown for electrolyte saturated with oxygen gas. The sLSV polarization curves recorded after the potential hold and coded in a grey scale based on E_d, clearly indicate that the hold experiments in Ar, H_2 and O_2 saturated electrolyte behave the same. The ORR start around 0.9 V_{RHE} with the freeing of Pt sites the same as the HOR. In addition, due to the sluggishness of completing a full OH adlayer a hysteresis between the sLSV and pLSV polarization curves is seen. Upon holding the potential, the steady state ORR current density decreases (see shaded area for the decrease in after 100 s) in the same manner as the HOR. Furthermore, the half wave potential E_{HW} of the ORR polarization curves after the potential hold clearly reflects a change above a hold potential E_d of 1.1 V_{RHE}, the potential region we associated with the formation of an oxide layer.

4. Conclusion

Our results demonstrate the well-known fact that in conventional cyclic voltammetry the investigated system is not at equilibrium conditions. In order to be able to study processes like the oxidation of a surface, the system must be given time to reach equilibrium coverage of oxygenated species. Hence instead of CV, a stripping technique was therefore used and combined with a probe reaction (HOR) for determining free Pt sites. Comparing the hold potential dependency of different key features, our analysis suggests that at quasi equilibrium conditions four potential regions can be separated where different oxygenated species dominate at the platinum surface. The oxidation process of Pt influences the probe reaction HOR in the same way as it influences the ORR. Below 0.7 V_{RHE} the Pt surface coverage of OH species is low and neither an influence on the HOR nor on the ORR is detected. Going to more positive potentials, OH_{ad} adsorption increases and at around 0.93 V_{RHE} a monolayer of OH_{ad} is formed blocking the Pt surface sites for both catalytic reactions. At further positive potentials, most likely OH_{ad} is gradually oxidized to O_{ad}. At 1.08 V_{RHE} the surface is fully dominated by O_{ad} and an oxidation process in form of PtO multilayer formation sets in. Applying voltammetry under non steady state conditions, these potential regions intermix.

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